

Solvent-Free Polymerization of Citric Acid and D-Sorbitol

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ABSTRACT: Copolymers of citric acid and D-sorbitol were synthesized with a solvent-free vacuum-oven synthesis with molar ratios of citric acid to D-sorbitol ranging from 1/1 to 6/1. The extent of the reaction was followed by the monitoring of the residual acid content of the system. As expected, the reaction occurred much more rapidly at 150 than at 110 °C. The Fourier transform infrared (FTIR) spectra of the products showed the expected FTIR bands at approximately 1735 and 1188 cm⁻¹, which were indicative of ester formation. Gel permeation chromatography showed a major product with a molecular weight of approximately 3500 Da. An insoluble material with a water-absorption index of up to 17 was also synthesized and could lead to possible applications as absorbers, thickeners, and biobased seed coatings. Additionally, the mono- and disodium salts of citric acid were also polymerized with D-sorbitol in a manner similar to that of the citric acid system. Soluble polymers were synthesized with a residual acid content of 5 mequiv/g of polymer. These materials showed Ca⁺²-sequestering ability (up to 0.56 mmol of Ca⁺²/g of the product). © 2006 Wiley Periodicals, Inc. *J Polym Sci Part A: Polym Chem* 44: 4259–4267, 2006

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INTRODUCTION

With global factors pushing the cost of crude oil past \$60 per barrel, the use of biobased feed stocks for the synthesis of materials has become more competitive. The use of renewable, bio-based agromaterials may be necessary to limit

the exhaustion of the Earth's reserves of nonrenewable resources. Current industrial biotechnology accounts for 5% of global chemical sales, but that number has been estimated to rise to as high as 20% by 2010.¹ Environmental factors are also important in our shift to a biobased industry, as shown by "The Green Chemistry Research and Development Act of 2004". Current practices need to be examined, and agriculturally based alternatives need to be considered.

One area of study is the use of citric acid and carbohydrates. Specifically, the U.S. Department of Agriculture and others have published reports of starch citrates,^{2–7} corn-fiber citrates,⁸ and cellulosic citrates.⁹ These anionic, cross-linked materials show promise as food thickeners, resistant starches, and ion-exchange res-

Product names are necessary to report factually on available data; however, the U.S. Department of Agriculture neither guarantees nor warrants the standard of the product, and the use of the name by the Department of Agriculture implies no approval of the product to the exclusion of others that may also be suitable.

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ins with metal-ion-binding ability. Water-soluble and/or network polyesters have also been prepared by the reaction of pure and partially neutralized citric acid with sorbitol,¹⁰ sugars and poly(vinyl alcohol),^{11,12} cyclodextrins,¹³ and gluconolactone.¹⁴ These reactions require the use of water or organic solvents to disperse the reactants. These products have potential uses as absorbers, thickeners, and water-transport seed coatings.¹⁵

D-Sorbitol has several advantages for this work. It has a low melting point (98–100 °C), which allows us to perform the reaction in a melt, possibly avoiding the addition of water, which is required when larger carbohydrates are used. D-Sorbitol is a reduced form of glucose, and it is readily available at a low cost. It has been used to synthesize polyesters with dicarboxylates such as divinyl sebacate¹⁶ and adipic acid,^{17–19} mostly through enzymatic catalysis.

Historically, citric acid was isolated from citrus fruits, but it is currently produced commercially by fermentation. Citric acid is a global product that is manufactured in over 20 countries. It is readily available, despite increasing consumption in the U.S. food and beverage industries, by which it is used widely for its flavoring and buffering properties. It is also used for its metal-chelating ability in the petroleum, industrial-cleaning, and cosmetics industries.

Citric acid and salts of citric acid are known to react with alcohols or polyols to form esters, even without catalysis.²⁰ The uncatalyzed polymerization is thought to go through a reactive anhydride and then react with the alcohol (Scheme 1, top reaction).² Copolyesters of citric acid and 1,2,6-hexane triol have also been cited as possible candidates for drug delivery.^{21–23}

The reaction of citric acid and D-sorbitol is expected to run without catalysis, forming the citrate sorbitol ester.⁹ The well-precedented anhydride formation of the sugar is also probable (Scheme 1),²⁴ with the 1,4-anhydrosorbitol ester, 1,5-anhydrosorbitol ester, and perhaps even 1,4,3,6-dianhydrosorbitol ester potential products.

Here the syntheses of citrate sorbitol copolymers with a simple vacuum-oven method with no added solvent²⁵ are reported. Key variables include the reaction temperature, time, water addition, and molar ratio of the comonomers. Additionally, sodium salts of citric acid were also used. The products were characterized by titration and Fourier transform infrared (FTIR) spectroscopy. Additionally, applicable samples were characterized with gel permeation chromatogra-

phy (GPC) and the determination of the water-absorption index (WAI) and Ca⁺²-sequestering ability.

EXPERIMENTAL

Materials

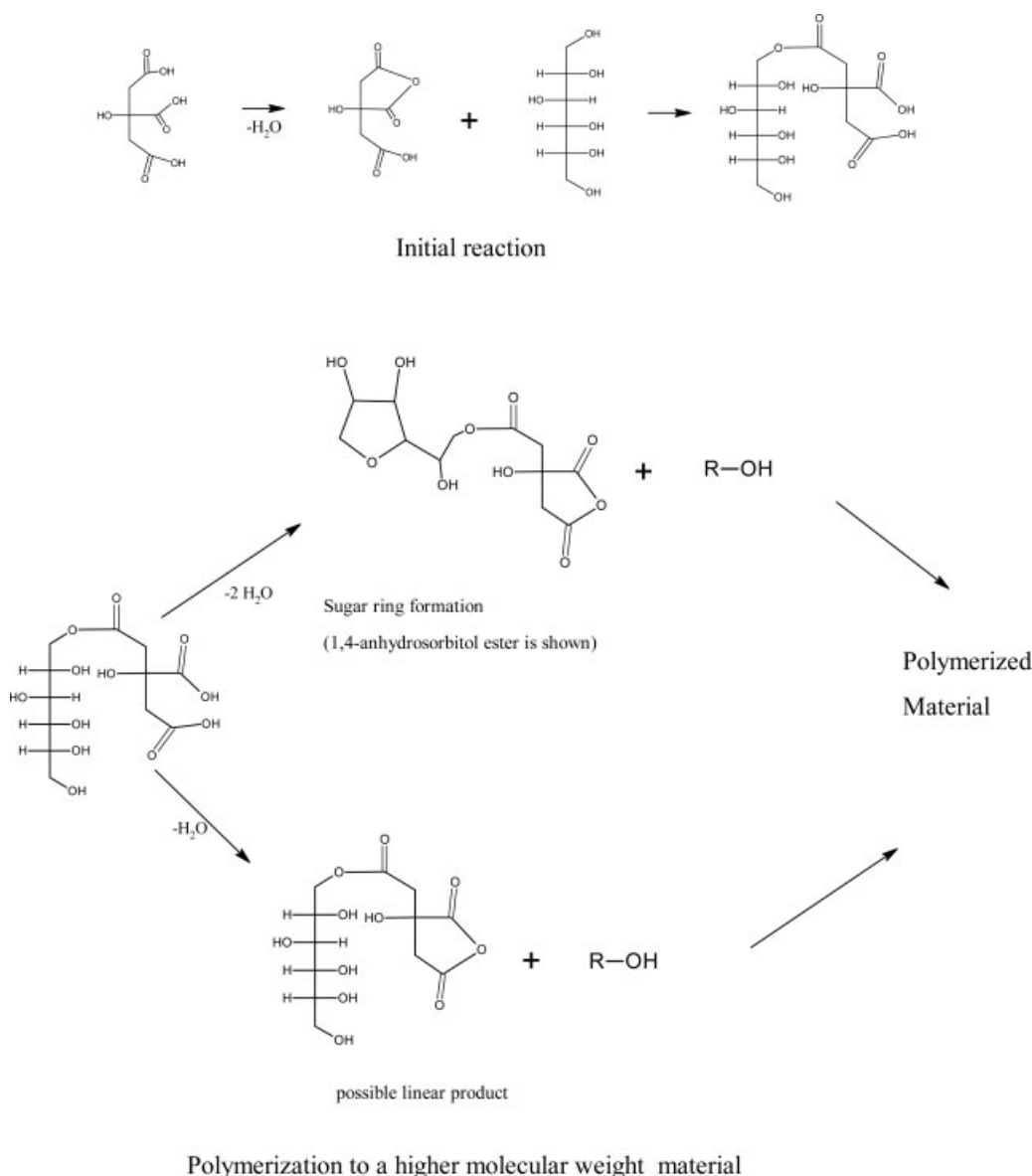
The following materials were used as received: D-sorbitol (Sigma; 98%), a sodium hydroxide standard solution (Sigma; 1.0 N), sodium chloride (NaCl; Fisher; ACS-certified), citric acid (Aldrich; 99%), sodium dihydrogen citrate (Aldrich; 99%), sodium hydrogen citrate sesquihydrate (Aldrich; 99%), calcium chloride dihydrate (CaCl₂; Fisher; ACS-certified), and a calcium standard solution (Cole-Parmer; calcium standard, 1000 ppm CaCl₂).

Instrumentation and Equipment

A Napco 5851 vacuum oven with a Welch W series 3 vacuum pump was used for the polymerization reactions. FTIR spectroscopy was carried out on a Thermo Nicolet Avatar 370 spectrophotometer with a transmission sample holder and standard potassium bromide pellets. GPC was performed on a Waters 1525 high-performance liquid chromatography (HPLC) system with a Waters 717 Plus autosampler and a Waters 2996 photodiode array detector and analyzed at 218 nm. A Phenomenex Poly-sep-GFC-P2000 column [molecular weight range = 0–9000 for poly(ethylene glycol)s] was used. NMR was performed on a Bruker Avance 500 NMR instrument operating at 500 MHz for ¹H and at 125 MHz for ¹³C. Bruker Icon NMR software was used on an HP x1100 Pentium 4 workstation. Peaks were referenced to sodium 3-trimethylsilylpropionate-2,2,3,3-*d*₄ at 0.0000 ppm. Simulations of ¹³C NMR spectra were performed by the ACD/CNMR predictor (version ACD/Labs 6.00) running on a Gateway Pentium 4 CPU with a 2.53-GHz processor. Ca⁺² titrations were performed with a Corning 350 pH/ion analyzer and a Cole-Parmer 27502-09 electrode without the use of an ionic strength adjuster.

Analysis of the Samples

GPC analyses were performed with an injection volume of 10 μL and a temperature of 30 °C. The HPLC system was set to an isocratic flow rate of



Scheme 1. Polymerization reaction of citric acid and sorbitol through an anhydride intermediate. Citric acid can then undergo further condensation, and the resulting crosslinking can give an insoluble material under certain conditions. Under most conditions, D-sorbitol can also lose water to also form an anhydride. (The terminal hydroxy group on the sorbitol is shown to react for clarity. A reaction at the other hydroxy groups can also occur.)

0.75 mL/min for a pH 8, 10 mM tris(hydroxymethyl)aminomethane, 100 mM NaCl aqueous buffer solution. The data were analyzed with the 218-nm wavelength. The molecular weights were calculated with sodium poly (acrylic acid) standards. The standards and soluble samples were dissolved in buffer solutions.

The WAI and water-solubility index (WSI) were measured by the weighing of a small

amount of a sample (~0.5 g) into a 50-mL centrifuge tube. After the addition of 25 mL of deionized water, the sample was stirred for at least 30 min. The pH was then adjusted to 7 with a 1.0 M NaOH solution, and this was followed by dilution to a final volume of 50 mL. The insolubles were separated by centrifugation, and the supernatant was removed with a pipette. The pellet was weighed, and WAI was

calculated as the ratio of the mass of the wet sample to the mass of the dry sample. The supernatant was dried *in vacuo* to a constant weight, and WSI was calculated as follows: $100 \times (\text{Mass of the dried supernatant} / \text{Mass of the sample})$.

The acid contents were determined by the addition of a sample to deionized water with stirring for at least 30 min. The samples were then titrated to pH 7 with a standard 0.2 N NaOH solution. Titrations were performed as rapidly as possible to minimize de-esterification.

Synthesis of the Polymers

A measured amount of D-sorbitol was melted in a 600-mL, glass beaker, and the desired amount of citric acid or sodium citrate salt was stirred into it. The total weights of the reactants were 20–30 g. The beakers were placed inside a vacuum oven, and the polymerizations were run at 110 or 150 °C. A vacuum of 30 inHg was maintained, except for the times during which samples were removed for analysis. There was no stirring during the reactions, except that produced by bubbling (the release of water). Reactions were repeated two to three times at 150 °C and once at 110 °C.

Ca⁺² Titrations

First, approximately 1 g of a sample was dissolved in 100 mL of deionized water. The pH was adjusted to 7.0 with a 1 M NaOH solution. The solution was left on a stir plate, and millivolt readings were taken with a Cole–Parmer Ca⁺²-selective electrode. CaCl₂ (0.5 M) was added in 100- μ L aliquots, and millivolt readings were allowed to stabilize and be recorded. Effective Ca⁺² concentrations were found by comparison with a standard log [Ca⁺²] versus millivolt plot. The endpoint was determined when the level of Ca⁺² detected was greater than 0.4 ppm. Calcium-sequestering values were calculated as millimoles of Ca⁺² added before the endpoint divided by grams of the sample.

RESULTS AND DISCUSSION

Synthesis with Citric Acid and D-Sorbitol

A polymer was synthesized with a solvent-free synthesis, in which D-sorbitol was first melted and citric acid was stirred into it. The mixture

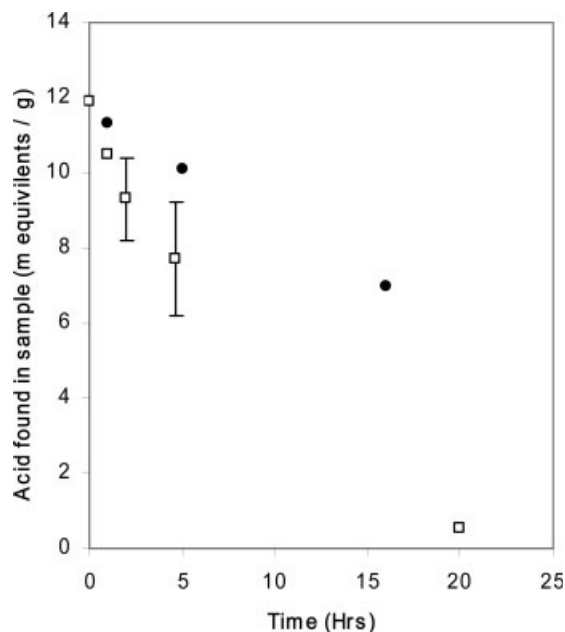


Figure 1. Amount of acid in a sample determined by the titration analysis of samples taken during the polymerization of 3/1 (mol/mol) citric acid/D-sorbitol. The reactions were run at (□) 150 and (●) 110 °C. The error bars represent standard deviations from the analysis of multiple (two to three) reactions. The error bars for short reaction times were similar to the size of the symbols.

was placed in a vacuum oven, and the temperature was increased to either 110 or 150 °C. The condensation reaction was followed by the titration analysis of samples taken at regular time intervals. As shown in Figure 1, the reaction was significantly faster at the higher temperature. With a 3/1 molar ratio of citric acid to D-sorbitol, the acidity of the mixture went from the theoretical value of 11.9 (mequiv of acid/g of material) to a value of 0.6 (mequiv of acid/g of material), demonstrating a nearly complete reaction of the acid groups. The material also changed during this time, from a completely water-soluble, sticky solid into a partially insoluble, yellow solid.

The reaction was also studied with FTIR spectroscopy. Neat citric acid (spectrum not shown) had C=O stretching peaks at 1754 and 1708 cm⁻¹ corresponding to free and hydrogen-bonded carboxyl groups.²⁶ After the reaction with sorbitol, the resulting spectrum (Fig. 2) exhibited bands at approximately 1735 and 1188 cm⁻¹, which were assigned to ester C=O stretching and C—O stretching, respectively.^{26,27} The weak band at 1406 cm⁻¹ was probably due to C—O stretching in unreacted citric acid.²⁶

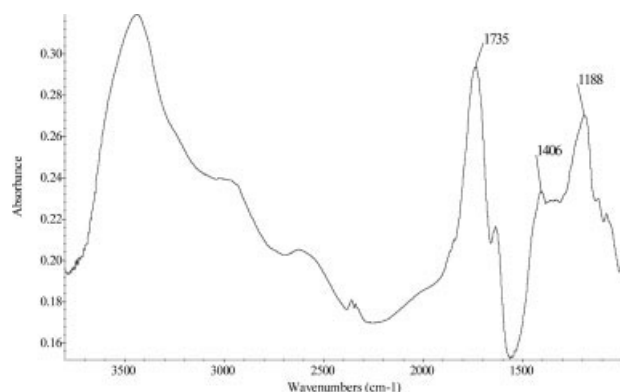


Figure 2. IR spectrum of a copolymer synthesized from a 3/1 (mol/mol) citric acid/D-sorbitol mixture *in vacuo* at 150 °C overnight.

With this reaction system, materials were synthesized with multiple molar ratios of citric acid to D-sorbitol ranging from excess hydroxyl groups (1/1 citric acid/D-sorbitol) to equal moles of acid and hydroxyl groups (3/1 citric acid/D-sorbitol; assuming no sugar anhydride formation) to a large excess of acid groups (6/1 citric acid/D-sorbitol). The products synthesized with a 3/1 or smaller citric acid/D-sorbitol ratio were partially insoluble, whereas the products with a 4/1 or greater citric acid/D-sorbitol ratio were completely soluble (Table 1). This was probably related to low levels of esterification in which the extent of the reaction was less than the value required for gelation. One interesting observation was that, despite the small carbohydrate used in the synthesis, the insoluble materi-

als displayed measurable water-absorption properties (Table 1), demonstrating possible use as biobased absorbents. The values of WSI and WAI were generally higher after adjustment to pH 7 because of neutralization of the free acid leading to polyelectrolyte effects (repulsion) and higher solubility and swelling. An exception was the 1/1 ratio, for which WAI decreased at pH 7 because of the very small amount of gel left after the pH adjustment.

It was possible to isolate a dry material with a high WAI by neutralization and separation of the soluble material from the insoluble gel. With a batch of the 3/1 ratio material, the gel was suspended in a large excess of water, and the pH was adjusted to 7 with a NaOH solution. The gel was separated by centrifugation, and the resulting solid was freeze-dried. WAI of this powder was tested, and a result of 17 was attained with a 200-mesh sieve to separate the gel from the sol phase.

Further insight into the swelling behavior was gained by a study of the soluble samples. GPC analysis was performed on polymers synthesized with a 5/1 ratio of the material at 2 and 4 h; both were completely water-soluble (Fig. 3). The results showed an increase in the material with a peak maximum molecular weight of approximately 3000 Da and additional material with a molecular weight of approximately 900 Da. These chromatograms demonstrated that approximately 54% of the material showed some molecular weight building to a level greater than or equal to 900 Da, while maintaining water solubility. This corresponded to a polymer with at least 5

Table 1. Observed Residual Acid, WAI, and WSI Values of Polymers Synthesized at 150 °C^a

Citric Acid/ D-Sorbitol	Residual Acid (m equiv/g)	Reacted Acid (%)	In Water		Adjusted to pH 7	
			WAI	WSI	WAI	WSI
Dry synthesis: 4-h reaction time						
1/1	2.6	68	3.4	66	2.9	96
2/1	3.9	63	5.1	51	11.8	64
3/1	6.9 (±0.7)	42 (±6)	6.0 (±1.1)	54 (±8)	9.4 (±2.6)	73 (±11)
4/1	9.5	25	Soluble	100	Soluble	100
5/1	10.2	22	Soluble	100	Soluble	100
6/1	10.8	21	Soluble	100	Soluble	100
Wet synthesis: 2-h reaction time						
3/1	5.0 (±0.9)	58 (±7)	4.7 (±1.8)	39 (±14)	8.7	39
Wet synthesis: 4-h reaction time						
3/1	3.8 (±0.1)	67 (±1)	2.8 (±0.5)	24 (±4)	7.4 (±1.3)	34 (±5)

^a See the Experimental section for the calculation of WAI and WSI. The standard deviations were determined from an analysis of multiple (two to three) reactions.

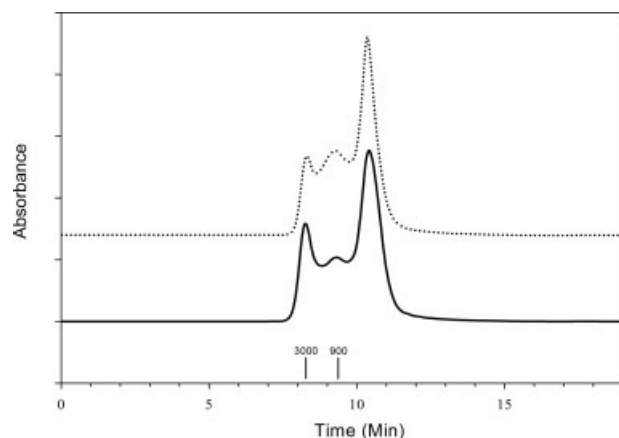


Figure 3. GPC chromatograms (normalized and offset for clarity) of the soluble material produced by the polymerization of a 5/1 (mol/mol) mixture of citric acid and D-sorbitol with reaction times of (---) 2 and (—) 4 h (see the Experimental section for the chromatography conditions).

and as many as 16 citric acid or D-sorbitol monomer units. Chromatographs of the soluble polymers made with a 6/1 molar ratio showed similar results, with 45% of the material having a molecular weight greater than or equal to 900 Da. The molecular weights given are based on linear sodium polyacrylate standards. Because sorbitol citrates are probably branched, the actual molecular

weights are probably higher than that of a linear polymer having the same hydrodynamic volume.

An examination of the carbonyl regions of the ^{13}C NMR spectra of D_2O solutions of soluble samples (150°C , 3-h reaction time; Fig. 4) supported the GPC results. About 50% of the signal intensity in the carbonyl region was composed of two signals at 177.6 and 174.4 ppm. These peaks were close to the literature values for unreacted citric acid (177.5 and 174.2 ppm).²⁸ A series of smaller peaks that were shifted slightly upfield by 1–2 ppm from the 174.4 and 177.6 ppm peaks were also evident. This was the expected shift predicted by the ACD/CNMR predictor for the conversion of citric acid into a mixture of citrate ester products. A similar result was obtained by the observation of the CH region of the spectra (30–45 ppm), in which the unreacted citric acid CH_2 carbons at 42.7 ppm also corresponded to about 50% of the total peak intensity of the region. As predicted, there were several signals shifted upfield by 1–3 ppm corresponding to citrate esters. Similar results were also obtained from the soluble 6/1 ratio system, although the amount of unreacted citric acid contributed approximately 67% of the peak intensity.

Sorbitol showed ^{13}C resonances at 65.8, 66.1, 72.9, 74.3, 74.5, and 76.1 ppm.²⁹ No sharp signals at 65.8 or 66.1 ppm (C1 and C6) can be

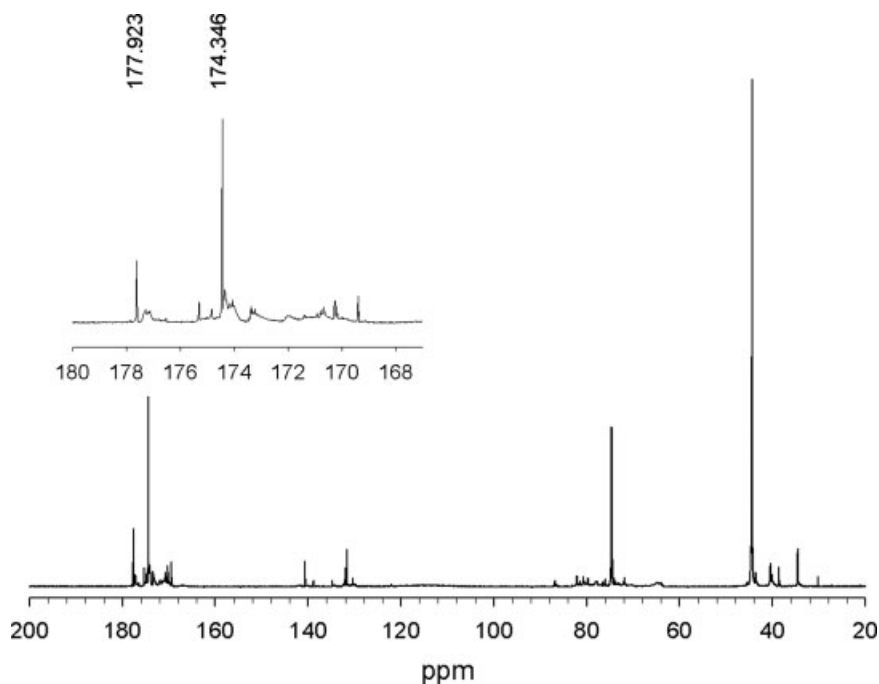


Figure 4. ^{13}C NMR spectrum and expanded carbonyl region of a D_2O solution of a polymer made with a 5/1 citric acid/sorbitol reaction.

seen in Figure 4, and this suggests that all the sorbitol reacted. The ACD/CNMR software predicted approximately 1 ppm downfield shifts upon esterification, and this was consistent with the broadening of several of the resonances in this region. Resonances in the 77–86 ppm range were assigned to ring carbons in 1,4- and 1,5-anhydrosorbitol (sorbitan), 1,4:3,6-isosorbide, and citrate esters thereof based on previous work³⁰ and the ACD predictor.

Small resonances can also be observed between 130 and 140 ppm in Figure 4. These were likely due to C=C carbons in aconitic and other acids formed by dehydroxylation and decarboxylation of citric acid at high temperatures.^{31,32}

Aqueous Synthesis

A copolymer was also synthesized by the dissolution of the reactants in water. Citric acid and D-sorbitol (3/1 ratio) were dissolved in a minimal amount of water and then dried in a forced-air oven at 80 °C overnight. The resulting solid was ground and then polymerized *in vacuo* at 150 °C. The resulting polymer displayed a WAI value within the experimental error of the dry synthesis (Table 1). The water solubility and acid titration values did show a larger extent of reaction in this system, probably because the reaction occurred during the drying process. Overall, there appears to be little advantage to dissolving the reactants in this system, although an aqueous system may be necessary to extend our reaction to higher melting carbohydrates.

Synthesis Using D-Sorbitol and Sodium Citrate

To synthesize a material that would remain soluble, similar polymerizations were performed with the various sodium salts of citric acid. Because the reaction pathway for the formation of citric esters may be through citric anhydrides, the sodium system should slow the crosslinking of the material, enabling the synthesis of a soluble material with the desired large carboxylate content and a fairly low number of sorbitol units.

Mixtures of disodium and monosodium citrate salts were made in the same manner as the citric acid system. The D-sorbitol was allowed to melt, and the citrate was stirred into it; the polymerization was conducted *in vacuo* at 150 °C. One difference between the citric acid and sodium citrate systems was the clarity of the melt at this stage. Citric acid and D-sorbitol formed a

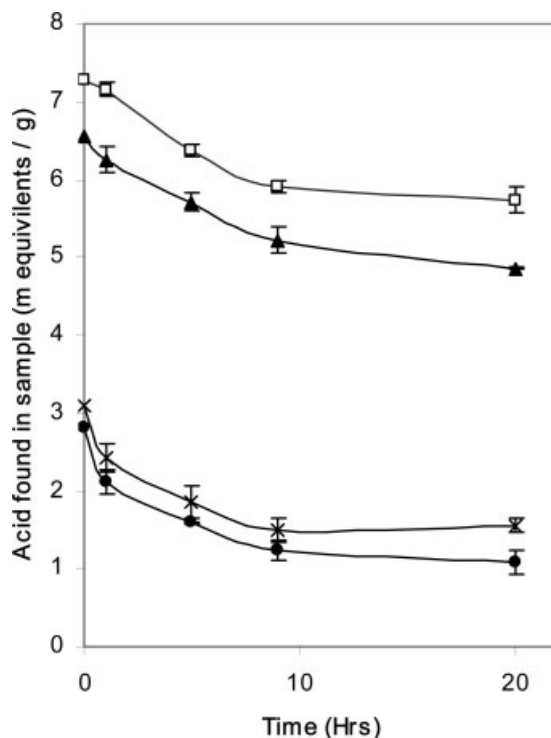


Figure 5. Acid content of samples taken during the polymerization of sorbitol with monosodium and disodium citrate at 150 °C: (x) 3/1 disodium citrate/D-sorbitol, (●) 2/1 disodium citrate/D-sorbitol, (□) 3/1 monosodium citrate/D-sorbitol, and (▲) 2/1 monosodium citrate/D-sorbitol. The error bars indicate standard deviations determined from two to three analyses of the same samples.

clear, viscous melt, whereas the sodium salts formed an opaque paste under the synthesis conditions. This suggests that sorbitol and sodium citrates are probably not completely miscible. Molar ratios of 2/1 and 3/1 were tried. The resultant polymers proved to be soluble as expected, and they contained a considerable amount of residual acid. FTIR spectra of sodium citrate and the sorbitol/sodium citrate reaction products (spectra not shown) both had C=O stretch peaks near 1730 cm⁻¹. A small peak at 1188 cm⁻¹ was observed for the sorbitol/citrate reaction products but not for the sodium citrates or sorbitol; this indicated that some esterification had occurred. Additionally, there were large absorbencies at 1581 and 1402 cm⁻¹ that were assigned to carboxyl anion antisymmetrical and symmetrical stretching modes.²⁶

As in the citric acid system, the reactions were titrated for the residual acid content (Fig. 5). As observed in the citric acid systems, the acid content of the samples decreased as the reaction

Table 2. Amounts of Calcium Added to the Solutions before the Level of Free Ions Reached 0.4 ppm^a

Sample	mmol of Ca ⁺² / g of Sample
Citric acid/D-sorbitol copolymer (5/1 mol/mol; 4-h reaction)	0.65 (±0.06)
Citric acid/D-sorbitol copolymer (4/1 mol/mol; 4-h reaction)	0.63 (±0.06)
Monosodium citrate/D-sorbitol copolymer (3/1 mol/mol; 9-h reaction)	0.56 (±0.12)
Monosodium citrate/D-sorbitol copolymer (2/1 mol/mol; 9-h reaction)	0.45 (±0.11)
Disodium citrate/D-sorbitol copolymer (3/1 mol/mol; 9-h reaction)	0.35 (±0.04)
Disodium citrate/D-sorbitol copolymer (2/1 mol/mol; 9-h reaction)	0.33 (±0.12)
Citric acid alone	1.3

^a This is a standard value for calcium-sequestering ability. The determination was performed at pH 7 by the titration of a sample with a CaCl₂ solution, and the endpoint was determined with a calcium-ion-selective electrode.

progressed. However, after about 9 h of reaction, there was no further loss of acidity in these systems, and this indicated that further polymerization was not taking place. Additionally, these samples were all soluble, with the exception of a small amount of an insoluble material after 20 h of polymerization. This was in contrast to the swellable network polymers observed in the citric acid system.

It was interesting to determine if these soluble polymers would retain enough carboxyl functionality to serve as ion binders. We measured the ability of the synthesized materials to sequester calcium ions with an ion-selective electrode. At pH 7, all of the materials displayed the ability to sequester calcium to a level below the detergency standard of 0.4 ppm (10⁻⁵ M) used in the literature (Table 2).³³ As expected, the amount of Ca⁺² binding increased with increasing citric acid concentration. This demonstrated that despite the consumption of carboxyl functionality used in the crosslinking reaction, there was still significant functionality remaining in the polymer. It also indicated a possible structural motif with at least 2 carboxylates in close proximity to each other,³³⁻³⁵ as seen in some oxidized sugars that also demonstrate Ca⁺²-sequestering ability.³⁶

CONCLUSIONS

This study has demonstrated the solvent-free synthesis of polymers of citric acid and D-sorbitol *in vacuo*. The synthesis reaction occurs at both 110 and 150 °C, but it is significantly faster at

the higher temperature. The molar ratio of the reactants is a major factor in the control of material properties such as solubility. A soluble material with a molecular weight of approximately 3000 was synthesized under conditions with a large excess of carboxylate groups; an insoluble polymer that absorbed up to 17 times its weight in water at pH 7 was also prepared. Soluble materials were also synthesized with the monosodium and disodium salts of citrate and D-sorbitol. This material had residual carboxylate groups, which could lead to applications as a detergent builder. Overall, this work has contributed to the understanding of the condensation polymerization of two biobased monomers and should help us shift toward the use of agricultural products in the biobased economy of the future.

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